I. Certain Physical Properties of Arsenic Trioxide in Water Solution

STANFORD UNIVERSITY LIBRARY
NOV 20 1925

II. The Action of Arsenic Trioxide in Water Solution on Certain Metallic Hydroxides

III. The Effect of Temperature on the Equilibrium Between Benzaldehyde and Benzoin

LEROY GRANVILLE STORY

A THESIS

Presented to the Faculty of
the Graduate College in the University of Nebraska
in Partial Fulfillment of Requirements for
the Degree of Doctor of Philosophy

3781
N36S
UNCLASSED
Dissertation

Department of Chemistry
Lincoln, Nebraska

1923

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

I. Certain Physical Properties of Arsenic Trioxide in Water Solution

II. The Action of Arsenic Trioxide in Water Solution on Certain Metallic Hydroxides

III. The Effect of Temperature on the Equilibrium Between Benzaldehyde and Benzoin

LEROY GRANVILLE STORY

A THESIS

Presented to the Faculty of
the Graduate College in the University of Nebraska
in Partial Fulfillment of Requirements for
the Degree of Doctor of Philosophy

Department of Chemistry

Lincoln, Nebraska

1923

The author wishes to express his sincere appreciation of the aid and encouragement given him in the work upon this thesis by Dr. Ernest Anderson.

I

CERTAIN PHYSICAL PROPERTIES OF ARSENIC TRIOXIDE IN WATER SOLUTION

Notwithstanding the enormous amount of investigational work on arsenic trioxide, some important physical properties of this substance are not accurately known. For this reason it seemed desirable to make determinations of the density, refractive index, solubility and hydrogen-ion concentration of equeous solutions of this substance as well as of the amount of arsenious acid formed in such a solution.

Purification of the Arsenic Trioxide

Arsenic trioxide was purified by recrystallization from hydrochloric acid as follows. Forty grams of the oxide was dissolved in 50 cc. of hot conc. acid, the solution diluted with 50 cc. of water, filtered immediately from any residue and 50 cc. more of water added to the filtrate.[1] The solution was cooled, and the crystals were filtered off and washed with ice water until free from chlorides. This procedure yields the octahedral form which was used in the investigation.

The Density and Refractive Index of Aqueous Solutions

The determination of the density of aqueous solutions was made at 25 ° by weighing a pycnometer full of water and afterwards full of the equeous solution of arsenic trioxide. The densities given are, therefore, referred to water at 25 ° as unity. When the density referred to water at 4 ° is desired it is necessary to multiply the densities given in Table I by the density of water at 25 °, that is 0.997077.

The determination of the refractive index was made at 22 ° by a sensitive Zeiss immersion refractometer. The data found are recorded in Table I, both in refractive indices and in scale readings.

[1] The statement of Wood, *J. Chem. Soc.*, **93**, 413 (1908), that As_2O_3 is least soluble in approximately 3.2 *N* hydrochloric acid was checked and found correct.

TABLE I

DENSITY AND REFRACTIVE INDEX OF AQUEOUS SOLUTIONS OF ARSENIC TRIOXIDE

As_2O_3 per liter of solution G.	Density at 25 ° Found	Density at 25 ° Calc.	Refractive index at 22 ° Found	Refractive index at 22 ° Calc.	Immersion scale reading 22 ° Found	Immersion scale reading 22 ° Calc.
1.796	1.0014	1.0014	1.33309	1.33305	14.71	14.71
3.212	1.0025	1.0025	1.33326	1.33324	15.15	15.17
3.580	1.0029	1.0029	.....	1.33328	.....	15.30
5.060	1.0039	1.0039	1.33348	1.33348	15.75	15.78
5.670	1.0044	1.0044	1.33355	1.33355	15.90	15.98
6.425	1.0050	1.0050	1.33363	1.33366	16.23	16.23
7.184	1.0057	1.0056	1.33376	1.33376	16.45	16.48
7.4366	.....	1.0058	1.33381	1.33380	16.60	16.57
8.561	1.0068	1.0068	1.33393	1.33394	16.89	16.93
10.13	1.0080	1.0080	1.33417	1.33415	17.53	17.46
11.35	1.0089	1.0089	1.33432	1.33431	17.93	17.86
12.85	1.0102	1.0100	1.33450	1.33452	18.38	18.35
14.368	1.0113	1.0112	1.33469	1.33471	18.88	18.85

All of the curves for the density, refractive index and scale reading plotted from the data in Table I are straight lines to which the equation $W = A + Bx$ applies, where W is the weight of material in grams per liter, A and B are constants and x is the density at 25 °, the refractive index at 22 °, or the immersion scale reading at 22 °. The values of the constants A and B determined as an average from Table I give Equation 1 where densities are used, Equation 2 where refractive indices are used and Equation 3 where scale readings are used.

$$\text{Equation 1: } W = -1288.36 + 1288.39x$$
$$\text{Equation 2: } W = -10062.7 + 7550x$$
$$\text{Equation 3: } W = -42.95 + 3.04x$$

A brief examination was made of the influence of temperature on the refractive index. The results showed that from approximately 21 ° to 27 ° each increase of 1 ° caused a decrease of 0.25 on the immersion refractometer scale or a decrease of 0.000097 in the refractive index.

Solubility in Water

Numerous investigators have studied the solubility of arsenic trioxide in water [2] but the results have been conflicting. Probably this is due in part to the fact that equilibrium is reached very slowly and in part to the use of different forms of the substance.

In this investigation, bottles containing water and excess of arsenic trioxide were shaken mechanically in a bath of boiling water until analysis showed that equilibrium had been reached.

[2] Clayton, *Chem. News*, **64**, 27 (1891). Chadounsky, *Chem. Centr.*, **1889**, 569. Winkler, *J. prakt. Chem.*, **31**, 247 (1885). Brunner and Talloczko, *Z anorg. Chem.*, **37**, 456 (190).

This required approximately two days. The solubility at lower temperatures was determined by placing the hot saturated solution in a thermostat at the desired temperature and shaking it until analysis showed that equilibrium had been reached. At 25° this required approximately 10 days while at 0° it required two weeks. As a check on some of these determinations, the solubility was also determined by mixing the trioxide and water, warming to the desired temperature and stirring until equilibrium was reached.

TABLE II

SOLUBILITY OF ARSENIC TRIOXIDE IN WATER

Temperature C.	As_2O_3 per 100 g. of H_2O Found G.	Calc. G.
0	1.21	1.21
15	1.66	1.64
25	2.05	2.05
39.8	2.93	2.85
48.2	3.45	3.40
62	4.45	4.45
75	5.62	5.63
98.5	8.18	8.18

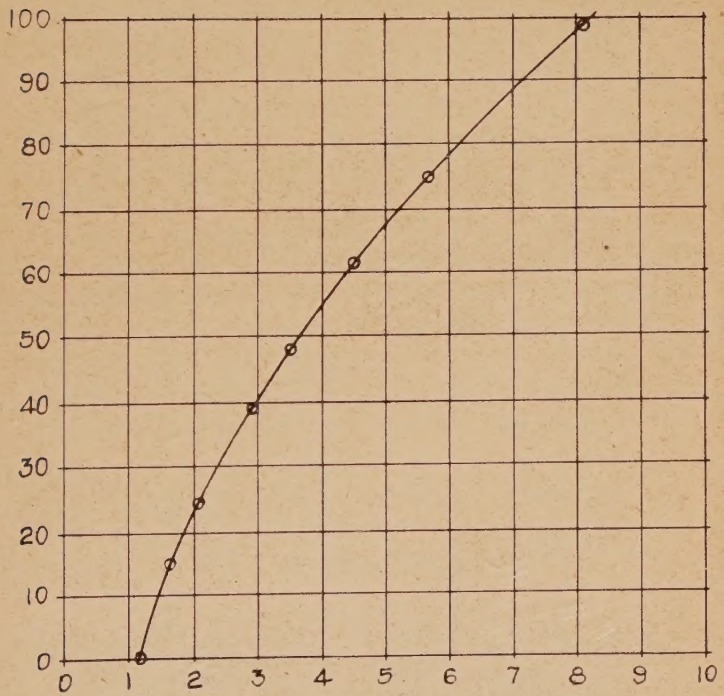

Fig. 1.—Solubility Curve for Arsenic Trioxide in Water

The dissolved trioxide was determined by weighing approximately 15 cc. of the solution, diluting and titrating the trioxide with standard iodine solution in the presence of sodium bicarbonate. The data obtained are recorded in Table II. The solubility curve plotted from these data is given in Fig. 1. It was found possible to represent this curve by the equation, $W = A + Bt + Ct^2$, where W is the weight of solute in g. per 100 g. of water, t is the temperature and A, B and C are constants whose values are, respectively, 1.21, 0.021 and 0.000505.

The Hydrogen-ion Concentration of a Water Solution of Arsenic Trioxide at 25 °

Numerous attempts were made to determine the hydrogen-ion concentration of a water solution of arsenic trioxide by means of the hydrogen electrode but the results were unsatisfactory, probably because of reduction of the substance.[3] The colorimetric method for determining hydrogen-ion concentrations [4] was finally used on a saturated solution in water. This gave a Sorensen value of 6.6 at 25 ° when either phenol red or bromothymol blue was used.

The Conversion of Arsenic Trioxide into Arsenious Acid

Zawidski found that the molecular weight of arsenic trioxide in water solution [5] was 101.5. The present investigation gave the molecular weight 92.5 by the boiling-point method and 99.17 by the freezing-point method. Apparently at 0 ° the trioxide is converted completely into some form of arsenious acid, possibly $HAsO_2$. Work is being continued on the application of the phase rule to the system, calcium oxide-arsenic trioxide-water and to other arsenites.

Summary

Accurate data are given for the density, refractive index, solubility, hydrogen-ion concentration and molecular weight of arsenic trioxide in water solution.

[3] Gladstone and Tribe, *J. Chem. Soc.*, **33**, 306 (1878). William Thompson, *Chem. News*, 99, 157 (1909).

[4] Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., 1920.

[5] Zawidski, *Bull. soc. chem.*, **30**, 1162 (1903); *Ber.*, **36**, 1427 (1903).

II

THE ACTION OF ARSENIC TRIOXIDE IN WATER SOLUTION ON CERTAIN METALLIC HYDROXIDES

Many arsenites have been described in the literature [1] some of which have a complex composition. Frequently these substances were prepared under conditions that might easily give rise to mixtures. Indeed the analyses of the products often do not agree with the formulas assigned to them. Biltz [2] studied the action of ferric hydroxide, aluminum hydroxide and silicic acid separately on water solutions of arsenic trioxide and found that no compounds were formed but absorption phenomena occurred. The results in the case of ferric hydroxide could be represented by an equation. The amounts of arsenic trioxide absorbed by aluminum hydroxide and silicic acid were very small and practically independent of the concentration of the arsenic trioxide in solution. These facts led to the investigation of the action of arsenic trioxide in water solution on certain metallic hydroxides in order to determine the composition of the products formed.

Since the method of procedure for studying systems similar to the above has been worked out and used by other investigators [3], it will not be described in detail. In general, varying weights of pure arsenic trioxide [4] and metallic hydroxide were placed in 250 cc. bottles containing approximately 200 cc. of water. The bottles were stoppered and mechanically shaken in a thermostat kept at the desired temperature until analyses showed that equilibrium had been reached. The solutions were then quickly filtered and the residue dried at room temperature. In each case the filtrate and residue were analysed for metallic oxide and arsenic trioxide and in some caces for carbon dioxide and water. The time required for equilibrium to be established varied with the temperature, ranging from three days at 99 ° to more than a week at lower temperatures.

The concentrations of arsenic trioxide in the filtrate were plotted as abscissae and the ratio of the percentages $\frac{As_2O_3}{MeO}$ in the precipitates as ordinates. When the resulting curve consisted of horizontal and vertical portions definite compounds were being formed. The composition of the compound corresponding to the horizontal portion of the curve is given by the value or the ordinate.

[1] Stavenhagen, *J. prakt. chem.*, **51**, 1 (1895); Reichard, *Ber.*, **27**, 1019 (1894), and **31**, 2165 (1898).

[2] *Ber.*, **37**, 3138 (1904).

[3] Miller and Kennrick, *J. Phys. Chem.*, **7**, 259 (1903). Allen, *Am. Chem. Jour.*, **25**, 307 (1901).

[4] Anderson and Story, *J. Am. Chem. Soc.*, **45**, 1103 (1923).

The System, Calcium Oxide-Arsenic Trioxide-Water

The data in this case, Table I and Fig. 1, prove conclusively that when mixtures of calcium hydroxide and arsenic trioxide are shaken in water at the temperatures 0°, 25° and 99°, two arsenites may result, depending on the concentration of the arsenic trioxide in the solution. When the concentration of arsenic trioxide in solution is 0.06 g. per 100 cc. at 25° (it would be 0.07 at 50° and 0.078 at 99°) or greater, calcium meta-arsenite, $Ca(AsO_2)_2$, in formed. On the other hand, when the concentration of arsenic trioxide in solution is less than 0.06 g. per 100 cc., basic calcium meta-arsenite, $Ca(OH)AsO_2$, results. This is clearly shown in Fig. 1. The first

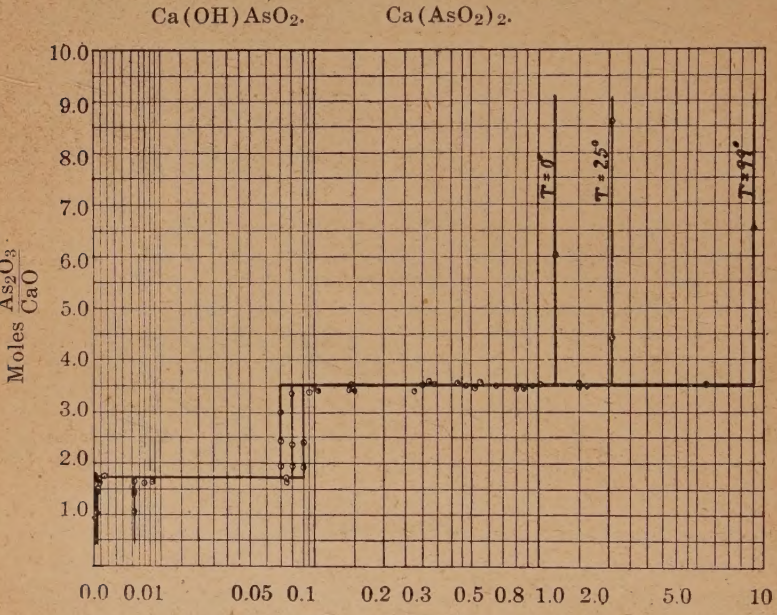

Fig. 1.—Curves for the system, CaO-As_2O_3-H_2O.

vertical part of the curve represents the solubility of the basic calcium meta-arsenite when excess calcium hydroxide is in the solid phase. As more arsenic trioxide is added to the solution the free calcium hydroxide disappears and we pass along the horizontal portion of the curve until the concentration of the arsenic trioxide becomes 0.06 g. per 100 cc. At this point calcium meta-arsenite begins forming. The second vertical portion of the curve represents a mixture of calcium meta-arsenite and basic calcium meta-arsenite, the meta-arsenite increasing in amount as the vertical part of the curve is ascended. The second horizontal portion of the curve

represents the formation of the meta-arsenite with increasing amounts of uncombined arsenic trioxide in solution. The third vertical sections of the curves represent saturated solutions of arsenic trioxide in water at that temperature and the points where free arsenic trioxide begins to appear in the solid phase.

TABLE I.

DATA FOR THE SYSTEM, CALCIUM OXIDE-ARSENIC TRIOXIDE-WATER

Total volume approximately 200 cc.

Ratio moles $\frac{As_2O_3}{CaO}$ in (1) $Ca(AsO_2)_2 = 3.53$, (2) $Ca(OH)AsO_2 = 1.76$

CaO used G.	AsO_3 used G.	Grams of As_2O_3 per 100 cc. of H_2O in solution	Moles $\frac{As_2O_3}{CaO}$ in solid	CaO used G.	AsO_3 used G.	Grams of As_2O_3 per 100 cc. of H_2O in solution	Moles $\frac{As_2O_3}{CaO}$ in solid
Temp. 0°				Temp. 25°			
1.00	1.00	0.0001	1.68	1.35	1.00	0.0002	0.96
1.00	1.00	.0001	1.70	1.00	1.30	.0002	1.38
				1.00	1.40	.0002	1.46
1.00	1.18	.0002	1.73				
1.00	1.30	.0003	1.70	1.00	1.48	.0003	1.68
1.00	1.40	.0004	1.70	1.10	1.77	.0009	1.65
1.00	1.50	.0006	1.72	1.00	1.77	.0660	1.74
1.00	1.90	.0016	1.76				
				1.00	2.00	.07	1.98
1.00	2.00	.06	1.98	1.50	3.54	.07	2.34
1.00	2.50	.06	2.40	1.10	3.54	.07	3.32
1.00	3.00	.06	3.00	1.20	4.00	.07	3.31
1.10	3.54	.10	3.42	1.00	3.54	.09	3.46
1.00	3.54	.14	3.32	1.00	3.60	.10	3.46
1.00	3.60	.15	3.33	0.85	3.40	.04	3.52
1.00	3.80	.28	3.32	.80	3.54	.52	3.48
1.00	3.90	.37	3.60	.59	3.54	.86	3.48
1.00	4.10	.43	3.52	.50	3.73	1.01	3.52
0.52	2.10	.55	3.60	.50	4.00	1.50	3.50
0.50	2.20	.66	3.50	.50	4.50	1.70	3.48
0.50	2.70	.93	3.50				
				50	5.50	2.21	4.40
0.50	5.00	1.23	6.00	.70	12.00	2.22	8.72
Temp. °99				Temp. 99° Cont.			
1.00	1.00	0.006	1.09	1.00	3.54	.30	3.51
1.00	1.18	.006	1.45	1.00	3.60	.34	3.53
1.00	1.20	.006	1.46	0.80	2.77	.47	3.50
1.10	1.50	.006	1.50	0.80	3.54	.80	3.40
				1.00	5.00	1.50	3.53
1.10	2.00	.006	1.70	1.00	10.00	5.60	3.53
1.00	1.50	.007	1.70				
1.00	1.80	.008	1.75	0.50	20.00	9.00	6.60
1.00	2.00	.08	1.91				
1.20	3.60	.08	2.38				

The System, Barium Oxide-Arsenic Trioxide-Water

Some difficulty was met in obtaining accurate data in this case but the results finally obtained, Table II and Fig. 2, prove that when mixtures of barium hydroxide and arsenic trioxide are shaken in water at the temperatures 25° and 50°, two arsenites may result, depending on the concentrations of arsenic trioxide in solution. Since the same compounds were formed at both temperatures, no experiments were made at other temperatures. An examination of Fig. 2 shows the presence of three vertical sec-

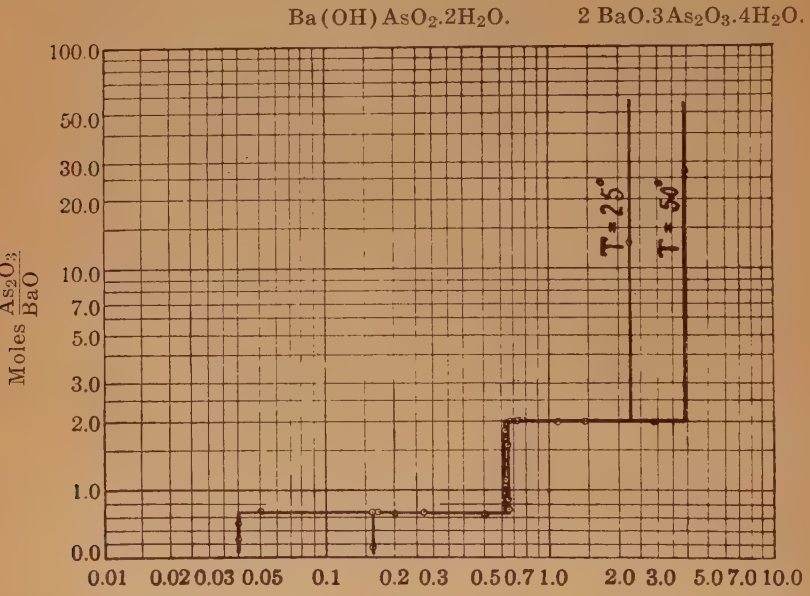

FIG. 2.—Curves for the system, BaO-As_2O_3-H_2O.

tions and two horizontal sections. The first vertical section represents the concentration of arsenic trioxide in solution when an excess of barium hydroxide is in the solid phase. As the concentration of arsenic trioxide is increased, the barium hydroxide disappears and leaves only hydrated basic barium meta-arsenate, $Ba(OH)AsO_2.2H_2O$, in the solid phase. When the concentration of arsenic trioxide reaches 0.6 g. per 100 cc. of solution, hydrated barium meta-arsenite, $2BaO.3As_2O_3.4H_2O$, begins to form. On increasing the concentration of arsenic trioxide, the basic arsenite disappears and we pass along the horizontal portion of the curve until the region of saturated solutions of arsenic trioxide in the presence of the meta-arsenite is reached.

TABLE II.

DATA FOR THE SYSTEM, BARIUM OXIDE-ARSENIC TRIOXIDE-WATER

Total volume, approximately 200 cc.

Ratio moles $\frac{As_2O_3}{BaO}$ in (1) $Ba(OH)As_2.2H_2O = 0.64$; (2) $2BaO.3As_2O_3,4H_2 = 1.94$

BaO used G.	As_2O_3 used G.	As_2O_3 per 100 cc. of solution G.	Moles $\frac{As_2O_3}{BaO}$ in solid	BaO used G.	As_2O_3 used G.	As_2O_3 per 100 cc. of solution G.	Moles $\frac{As_2O_3}{BaO}$ in solid
	Temp. 25°				Temp. 50°		
19.20	4.00	0.04	0.29	19.20	1.00	0.16	0.168
13.44	4.00	.04	.53				
				19.20	4.00	.16	.66
9.60	4.00	.05	.70	13.44	4.00	.17	.64
5.76	4.00	.50	.64	9.60	4.00	.20	.62
				6.70	4.00	.27	.67
2.40	1.50	.63	.96				
4.80	4.00	.63	1.06	5.76	4.00	.67	.74
3.84	4.00	.63	1.12	4.80	4.00	.66	.82
1.44	2.00	.63	1.72	3.84	4.00	.65	1.10
3.84	6.00	.63	1.82	3.84	6.00	.66	1.66
0.96	2.00	.73	2.00				
3.84	8.00	.75	2.08				
0.67	3.00	1.15	2.00				
0.96	4.00	1.45	2.01				
6.68	10.00	2.30	13.17				

The System, Lead Oxide-Arsenic Trioxide-Water

Lead hydroxide was prepared by precipitating a weighed amount of lead nitrate with ammonium hydroxide. The precipitate

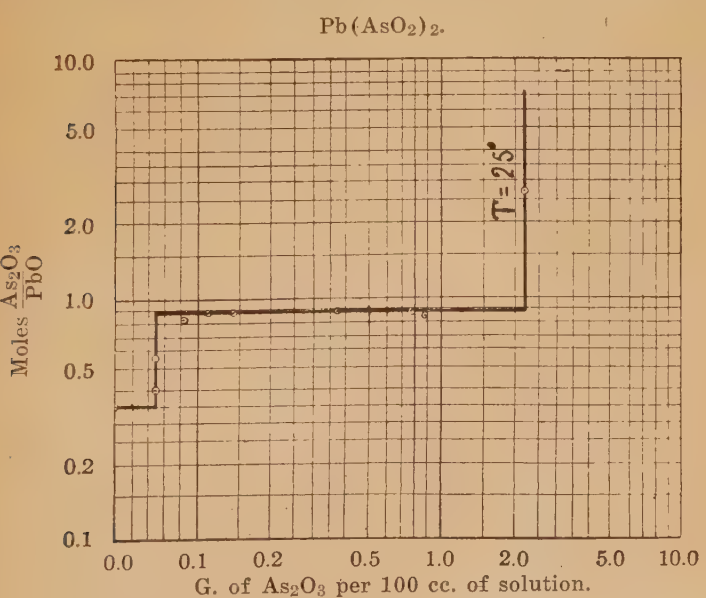

FIG. 3.—Curve for the system, PbO-As_2O_3-H_2O at 25°.

was washed repeatedly by decantation and treated with arsenic trioxide as described above. The data obtained, Table III and Fig. 3, prove conclusively that when excess arsenic trioxide is used, lead metarsenite, $Pb(AsO_2)_2$, is formed. There are indications that basic lead arsenite is also formed when excess lead hydroxide is used, though because of experimental difficulties this latter was not obtained in a form suitable for analysis.

TABLE III.

DATA FOR THE SYSTEM, LEAD OXIDE-ARSENIC TRIOXIDE-WATER

Total volume, approximately 200 cc.

Radio, moles $\frac{As_2O_3}{PbO}$ in $Pb(AsO_2)_2 = 0.89$

$Pb(OH)_2$ used G.	As_2O_3 used G.	As_2O_3 per 100 cc. solution G.	Moles $\frac{As_2O_3}{PbO}$
		Temp. 25°	
1.40	0.430	0.002	0.35
1.40	.602	.049	.40
1.40	.774	.048	.56
1.40	1.29	.088	.83
1.40	2.58	.770	.89
1.40	1.72	.329	.89
1.40	1.03	.140	.89
1.40	3.44	1.120	.89
1.40	6.00	2.200	2.64

The System, Magnesium Oxide-Arsenic Trioxide-Water

In this case freshly precipitated magnesium hydroxide was prepared by mixing water solutions containing equivalent amounts of potassium hydroxide and magnesium sulfate. The precipitated magnesium hydroxide was washed repeatedly by decantation before mixing with arsenic trioxide. Preliminary determinations showed that 1 g. magnesium hydroxide removed approximately 0.12 g. arsenic trioxide from aqueous solution of the latter irrespective of the concentration. Since this amount was too small for the formation of any arsenite the general method of procedure was varied in this case.

An accurately determined amount of the gelatinous magnesium hydroxide, 1.035 g., was mixed with 200 cc. of water in which varying amounts of arsenic trioxide, accurately weighed, had been previously dissolved. The mixture was shaken until analysis showed equilibrium had been reached. The arsenic trioxide remaining in solution was determined and that absorbed by the magnesium hydroxide calculated. The data, Table IV, show that 1.035 g. magnesium hydroxide absorbs approximately 0.12 g. arsenic trioxide from aqueous solutions of the latter irrespective of the concentration.

TABLE IV

DATA FOR THE SYSTEM $MgO--As_2O_3--H_2O$

Total volume 200 cc.

Weight of $Mg(OH)_2$ Used G.	Weight of Dissolved As_2O_3 Used G.	Weight As_2O_3 Remaining in Solution G.	Weight As_2O_3 Absorbed by 1.035 g. $Mg(OH)_2$ G.
1.035	0.0664	0.014	0.052
1.035	0.1328	0.045	0.088
1.035	0.1992	0.095	0.104
1.035	0.2656	0.153	0.113
1.035	0.332	0.210	0.122
1.035	0.664	0.540	0.124
1.035	1.328	1.200	0.128
1.035	1.992	1.87	0.122
1.035	4.928	4.80	0.128

Summary

The systems $CaO--As_2O_3--H_2O$; $BaO--As_2O_3--H_2O$; $PbO--As_2O_3--H_2O$ and $MgO--As_2O_3--H_2O$ were studied. In the first three systems definite arsenites were obtained with the following formulas: $Ca(OH)AsO_2$; $Ca(AsO_2)_2$; $Ba(OH)AsO_2.2HO$; $2BaO.3As_2O_3.4H_2O$ and $Pb(AsO_2)_2$. In the last system no arsenite was formed but an absorption of the arsenic trioxide by the magnesium hydroxide resulted.

III

THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM BETWEEN BENZALDEHYDE AND BENZOIN

Introduction

Anderson and Jacobson have shown that the benzoin condensation is reversible[1] and that in alcohol solution in the presence of sodium cyanide the equilibrium constant[2] between benzaldehyde and benzoin is approximately 0.245 at 79 °. In order to determine the effect of temperature on the equilibrium the investigation described below was carried out.

The method used in determining the point of equilibrium was to dissolve accurately weighed amounts of benzoin and benzaldehyde in a definite volume of 95% alcohol, add NaCN, heat to the described temperature for a short time and determine the amount of benzoin present in the mixture. When the weight of benzoin recovered was the same as that used the benzoin and benzaldehyde were in equilibrium. In practice a constant volume of alcohol, 220 cc., and a constant weight of benzoin, 5 g. were used and the weight of benzaldehyde varied. Two weights of benzaldehyde were thus obtained, one of which gave a slight increase and the other a slight decrease in the weight of benzoin.

1. *J. Am. Chem. Soc.*, **45**, RCF (1923); Stern, Z, *physik. Chem.*, **50**, 526, 1904; Lachman, *J. Am. Chem. Soc.*, **45**, 1529 and 1533 (1923).

2 Lachman (*loc. cit.*) pointed out that Anderson and Jacobson (*loc. cit.*) overlooked the very careful work of Stern (*loc. cit.*) on the velocity of the benzoin condensation. It is needless to say this was unintentional on the part of the authors. Stern mentioned that the benzoin condensation is reversed by potassium cyanide in alcohol solution but he failed to point out the importance of this for his own work. He did not mention the reversal of the condensation in the summary of his work and the abstracts of his work in the *J. Chem. Soc.*, **88** (2), 150 (1905) and *Chem. Cent.*, 1904 II, 835 do not mention it. Bredig and Stern [*Z. Electrochem.*, **10**, 582 (1904)] in the report on Stern's work do not mention the reversal of the condensation.

Stern states that his values for the velocity constant, K, of the benzoin condensation are not constant but decrease as the reaction proceeds. [*Z. physik. Chem.*, **50**, 525-528, 533 (1904)]. If an equilibrium exists between benzaldehyde and benzoin the value of K as determined by Stern should not be constant but decrease. As the reaction proceeds and increasing amounts of benzoin are formed the reverse reaction would gradually increase. This would cause a corresponding decrease in the value of K, just as Stern found experimentally to be the case. Stern's explanation that the decrease in K is due to decomposition of the potassium cyanide may also in part be true. Both causes would have the same effect and both may contribute to the observed decrease in K.

As noted by Stern (*loc. cit., p.*), and by other investigators, certain side reactions remove some of the benzoin and benzaldehyde and thus disturb the equilibrium. It is thus not a true equilibrium (*Lachman, loc. cit.*). However the data in this paper show that under the conditions of the experiment at any moment the benzoin and benzaldehyde are in equilibrium since a slight increase or decrease in the concentration of one causes a corresponding shift in the equilibrium.

From these data the exact weight of benzaldehyde that would cause no change in the weight of benzoin used could be calculated.

Experimental Part

Five grams of pure benzoin and varying amounts, accurately weighed, of pure benzaldehyde were made up to 200 cc. with 95% alcohol. This solution was poured into a 700 cc. Erlenmeyer flask and 20 cc. additional alcohol used for washing out the volumetric flask. The solution was heated to the desired temperature, 2 g. of 98% NaCN added, and the heating continued for 5, 10 or 15 minutes in an atmosphere of nitrogen. In the experiments at 50 ° and 60 ° the heating was for 15 minutes, in those at 70 ° it was for 10 minutes while in those at 79 ° it was for 5 minutes. The solution was then diluted with an equal volume of ice water, cooled to 20 °, and kept at this temperature for 10 minutes. The precipitated benzoin was filtered off on a weighed filter paper, washed with 50% alcohol that had been previously saturated with benzoin, dried and weighed. To the weight of benzoin recovered was added 0.44 g., i. e. the weight of benzoin remaining dissolved in 440 cc. of 50% alcohol at 20 °. Table I is a summary of the experimental results.

The Equilibrium Constant

The equilibrium constant may be calculated by substituting the experimental data recorded in Table I in the equilibrium constant formula for a reaction of the type $2A \rightleftarrows B$. This formula is $K = \frac{A^2}{B}$ where A and B are expressed in gram mols per liter of solution. The constants found are recorded in Table I.

TABLE I

DATA ON THE EQUILIBRIUM BETWEEN BENZALDEHYDE AND BENZOIN AT DIFFERENT TEMPERATURES

Total volume 220 cc.

Temp.	Benzoin Used G.	Benzaldehyde Used G.	Benzoin Found G.	Increase in Benzoin G.	Benzaldehyde in equilibrium with benzoin used G.	K Found	K Calc.
40 [3]	3	8.28	3.02	+0.02			
40	3	8.00	2.96	−0.04	8.14	1.89	1.793
50	5	7.77	5.084	+0.084			
50	5	7.28	4.884	−0.116	7.60	0.99	1.034
60	5	6.09	5.058	+0.058			
60	5	5.98	4.94	−0.06	6.03	0.623	0.623
70	5	4.89	5.058	+0.038			
70	5	4.39	4.954	−0.046	4.70	0.378	0.386
79	5	3.90	5.10	+0.10			
79	5	3.55	4.95	−0.05	3.66	0.230	0.2548
82	5	2.99	5.10	+0.10			
82	5	2.47	4.965	−0.035	2.60	0.116	0.223

[3] The experimental data at 40 ° may be slightly inaccurate.

From the heats of combustion of benzaldehyde and benzoin given in standard tables of constants, and the equilibrium constant K at one temperature, the values of K at other temperatures can be calculated by means of the Van't Hoff equation:

$$\text{Ln}\frac{K_2}{K_1} = \frac{-Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The value 10900 calories was used for Q in calculating the values of K recorded in the last column of Table I. It is assumed that this value remains constant over the range of temperature investigated. The agreement between the calculated and determined value of K is very close in view of the fact that the value of Q is derived from average heats of combustion whose extremes are rather large.

Work is being continued on the constant at higher and lower temperatures as well as on the equilibrium constant for other closely related reactions. In a later communication when more data are available an explanation will be offered for the deviation between the experimental and calculated values of K.

Summary

The value of the equilibrium constant between benzaldehyde and benzoin has been determined at six different temperatures and found to agree fairly closely with the calculated values.

(5575-25)